PRIMARY DISINFECTANTS IN DRINKING WATER

- ALTERNATIVES & THEIR CHARACTERISTICS

Don Gates, Ph.D

Sacramento CA

For Vermont Agency of Natural Resources

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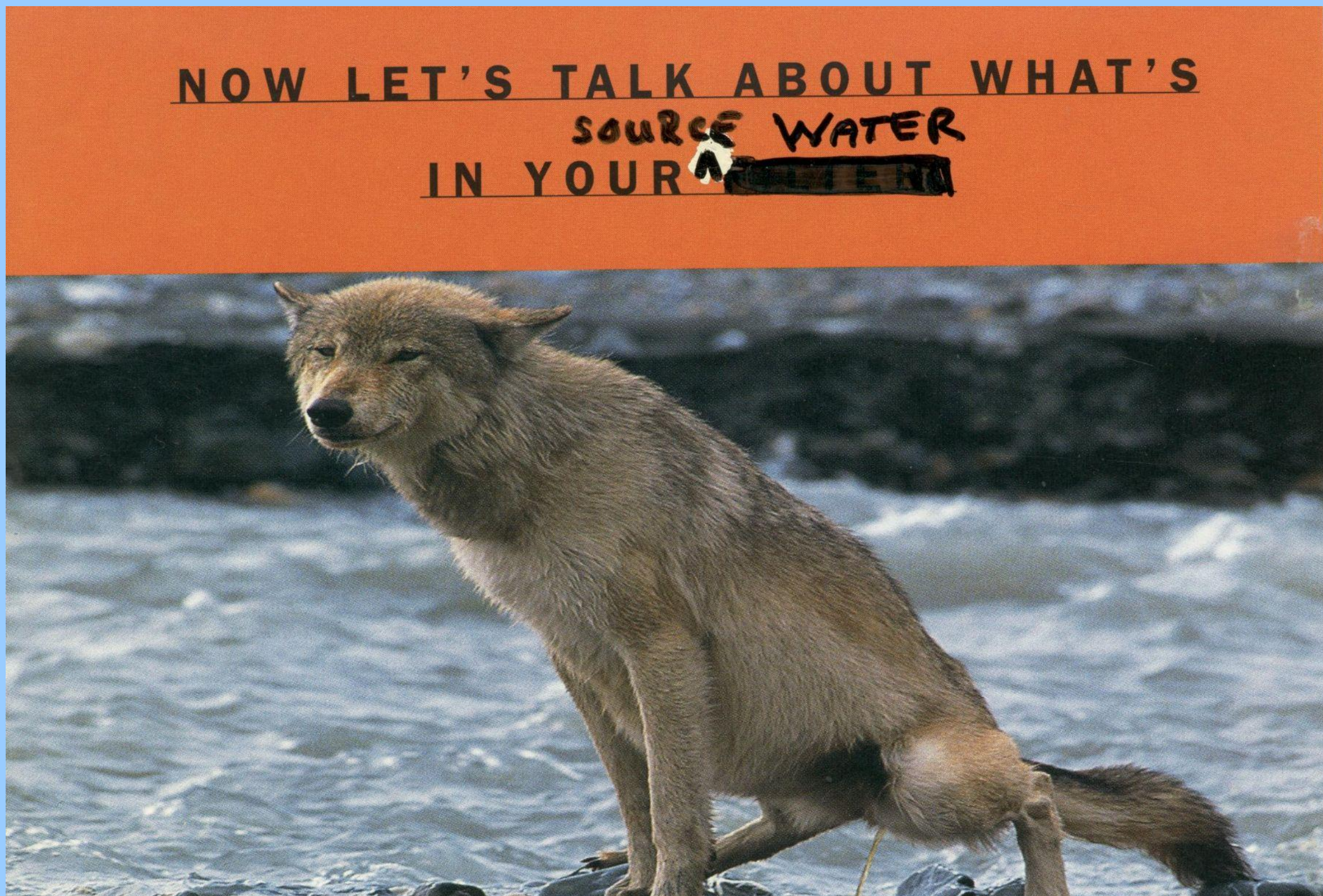
SOURCE WATER QUALITY



Source Water Quality

- Tremendous national variations
- Watershed protection & uses
  - E.g. Agriculture, cattle
  - Recreational use
- Assessment programs to identify source characteristics & contaminants
- NOM (Natural organic matter)
  - E.g. Humic substances,
- Seasonal growth impacts
  - Blue-green algae; Nostoc
  - Effect on manganese loading
  - Foliage or ice/winterkill
- Effects of rapid changes on treatment (e.g. spring runoff)
- Geology & local features
  - Lake, river, impoundments,
  - ground water (UI)

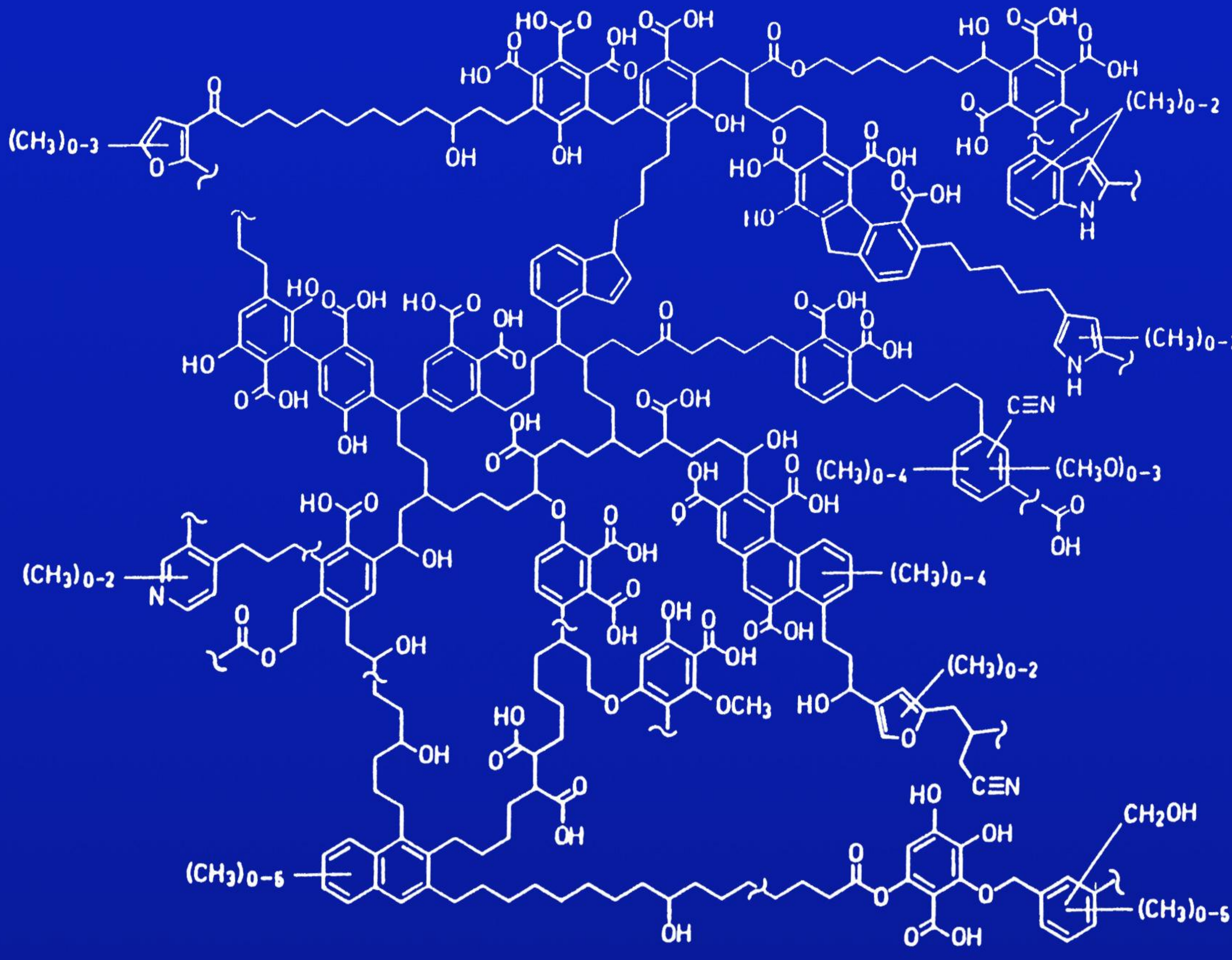


Fig. 12.7 Chemical network structure of humic acids according to Schulten and Schnitzer.[7] Reproduced by permission of Springer-Verlag.

DBP’s

- Many “oxidation byproducts” are common to all of the oxidative- disinfectant choices
- Halogen-substituted DBP’s are the easiest ones to find and measure
- Over 600 DBP’s have currently been identified

THE ALTERNATIVES

- **CHLORINE – the accepted standard -** Cl_2
  - **Gas/liquid, aqueous (bleach), hypochlorite salts,**
  - **electrochemical generation from (purified) brine**
- **AMMONIA – CHLORINE PROCESS**
  - **process favoring formation of chloramines** NH_2Cl
- **CHLORINE DIOXIDE** ClO_2
  - **Generated from chlorite or chlorate salts**
  - **or electrochemically from brine (as acid) or chlorite**
- **OZONE** O_3
  - **Generated by corona discharge from LOX (O_2)**
  - **purified, dried air**
  - **Or VUV (190-200 nm) lamps**
- UV (**additional inactivation to chemical)** UV_C
  - **From low & medium mercury lamps**

Disinfectants

Agent	Shipping	Storage & handling	Generation	Regulatory & industry
Liquid Chlorine	Approved but future concerns	Headers & evaporators; Future DHS rules	N/A	CI, AWWA MOP NSF certification Standard B300, GRAS – OPP
Hypochlorite salts (and Ammonia for chloramines)	Approved	Aqueous solutions chemical & acid-resistant pumps, containment for extra chemicals	Purified brine is needed for on-site electrochem. MCA forms rapidly & spontaneously in dilute solutions	CI, B300(04), Aqua (& other) ammonia: B302,5,6(07)
Chlorine dioxide	Not permitted	A few batch types for a few hours. Pumped/ educted. 30 days precursor storage required.	Chlorite-based, with Cl_2 gas or bleach + acid; electrochemical and only one chlorate-peroxide-acid based system.	AWWA B303(05) NO standard for ClO_2 purity, some vendors lack any “moral compass” OPP registration!

Disinfectants (cont'd)

Disinfectant	**Shipping**	**Storage & handling**	**Generation**	**Regulatory & industry**
Ozone	No	Educted as a gas in air or O_2, High efficiency ejectors; Prep Gas storage	Dried & purified air or LOX feed. *Corona discharge* from dielectrics or UV_D lamp	•NSF cert, •IOA & AWWA Vendors provide excellent support • Diffusers & Contactors
UV_C • 254 nm • 240 -315 nm	N/A	Maintenance & bulb replacement, high turbidity & -fouling	Medium & low pressure mercury lamps	•NSF certification •IUVA •Vendors provide Excellent support

Chlorine Terminology

- Chlorine as molecular gas (Cl_2) ***hydrolyzes*** in water
  $$Cl_2 + H_2O \rightarrow HCl + HOCl \quad (T_{1/2} \sim 3 \text{ msec})$$
- Depending on pH, these subsequently ***ionize*** to form their ***conjugate acid-base*** pair
  - Hypochlorous acid (HOCl) and Hypochlorite ion (OCl^-)
  - Cl^-, H^+ (as H_3O^+ proper) and OH^-
  - This specific pH for 50% of each species is the ***pKa***
  - pKA is 6.8 for [$HOCl/OCl^-$] and 7.0 for water
  - All ionic species (including organics) have a pKa

Chlorine Oxidative Species –
a.k.a. “Interoxy halides”

Oxidation state	**Species name**	**Formula**	**pKa**
-1	Chloride	Cl-	N/A
0	Chlorine (molecular)	Cl_2	N/A (<pH 2)
+1	Hypochlorous acid - hypochlorite ion	HOCl & OCl^-	pH 6.8
+2	Chlorine monoxide	Cl_2O	Free radical
+3	Chlorous acid/chlorite	$HClO_2$ & ClO_2^-	< pH 1.7
+4	Chlorine dioxide	ClO_2	Free radical
+5	Chloric acid/chlorate	$HClO_3$ & ClO_3^-	< pH 1.7
+6	(Chlorine trioxide)	ClO_3	Radical
+7	Perchloric acid - perchlorate ion	$HClO_4$ & ClO_4^-	< pH 2

Chlorine Species (around water)

- **Molecular chlorine** (Cl_2) (gas from liquid) ➔
- Changes In Aqueous Solutions (low pH) after ejector/dilution into water (except @ < pH 2)
  - ~6 g/L from Cl_2 gas
- Or as hypochlorite salts (stored @ high pH for stability)
  - Bleach – sodium hypochlorite
    - Trade %'s up to ~20%
  - Javelle water
  - Chlorine water

- **Chloramines:**
- Formed favorably under dilute reactions between NH_3^+ and HOCl/OCl^-
- Monochloramine
  - (MCA or NH_2Cl)
- Dichloramine ($NHCl_2$)
- Trichloramine ($NHCl_3$)
  - nitrogen trichloride
  - gas, but only at low pH
- Organic chloramines

BREAKPOINT CHLORINATION

- Overcome oxidant (organic and/or inorganic) demand to establish residual (C) disinfectant level
- For chloramination, dose ammonia and chlorine at levels to favor ***monochloramine*** formation

$NH_3^+ \ + \ OCl^- \rightarrow \ NH_2Cl \ \ (+ H_20)$

$\rightarrow$ (XS OCl^-) $\rightarrow$ $NHCl_2$

$\rightarrow$ (XS $OCl^{-)}$ $\rightarrow$ NCl_3

$\rightarrow\rightarrow$ HOCl / OCl^-

+ X-DBP’s

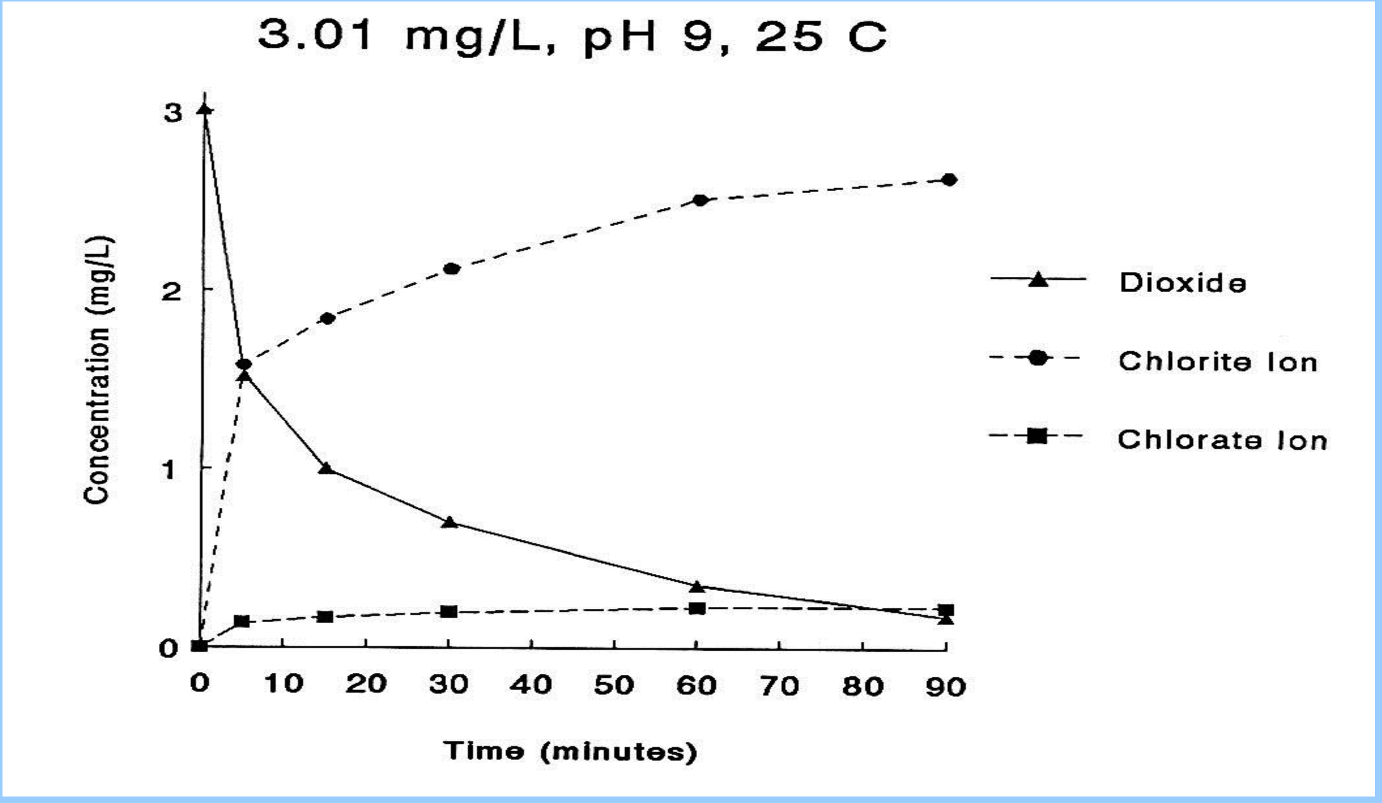
OXIDANT “DEMAND”

Generally, on a mass basis,
the “Oxidant Demand”
is far greater than the
“disinfection demand requirement ”
for inactivating biological contaminants
in source and process waters.

OXIDANT DEMAND

- Varying constituents make up ‘oxidant demand’ mass in the source water
  - Mostly organic and inorganic moeties in source waters
  - Biological/microbial components are ***a small percentage*** of mass, but dominate the risk elements
- Normal procedure is to add sufficient oxidant to overcome demand – very complex kinetics
  - **NOTE**: Oxidation to extinction (CO_2 and H_2O) is not possible
- Modification of soluble phase constituents by oxidation often aids coagulation & clarification process
  - Reducing organic loading prior to adding disinfectant can reduce the levels of DBP precursors

Typical ClO_2 Profile
(from Bubnis, et.al. AWWARF, 2008)
Demand Concept 1



TERMINOLOGY (cont'd)

- ***Oxidation (LEO) & Reduction - (GER)***
- ***"Re-dox" reactions:***
  - Many are going on at the same time in this complex matrix
  - "Simple" chemical reaction equations are a means to indicate one (or very few) of the many components.
- ***Free Radical*** :
  - compound or species which has an unpaired electron in its outermost shell
- ***Kinetics & thermodynamics:***
  - Reaction rates and equilibrium constants, effects of pH, temp and concentration, reaction half-lives, pKa's, end-product inhibition or soluble phase changes –------ optimal conditions
  - all will affect the reactions that go on (some favorable, some not) not merely the ***oxidation potential*** of a half-reaction.

Oxidant Characteristics

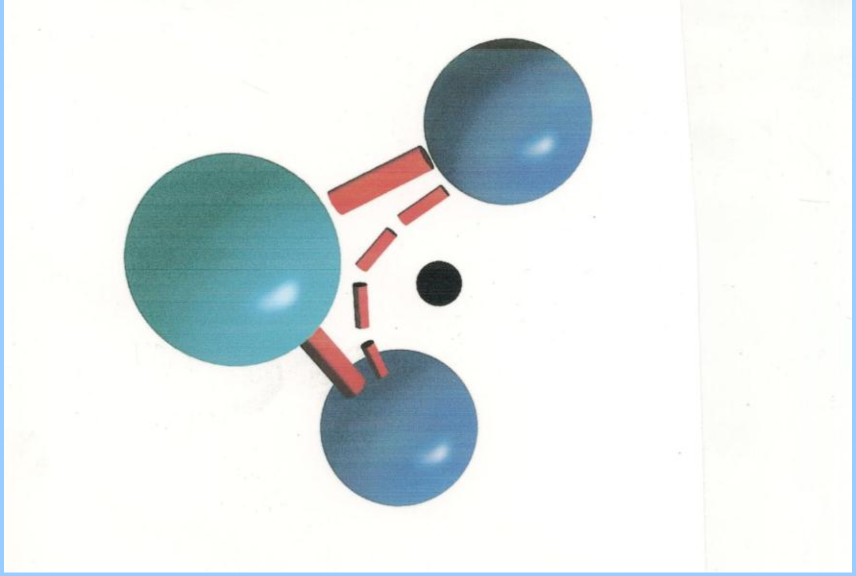
SPECIES	E^o	E^{o}@pH7	Solubility	D. Efficacy
OH• Hydroxyl radical	2.80		(short half-life)	n/a
O_3 Ozone	2.07	1.59	Very Low	+++++
H_2O_2 Peroxide	1.77		High	Poor - n/a
HClO Hypochlorous	1.49	1.28	High	+++
ClO_2 Dioxide	0.95	0.95	Very high	+++ -
ClO^- Hypochlorite	0.90	0.49	High	++
ClO_2^- chlorite ion	0.78	0.37	High	+
NH_2Cl MCA	1.16	0.62	High	++
I_2 Iodine	0.62	0.62	High	++ -

Terminology – cont'd

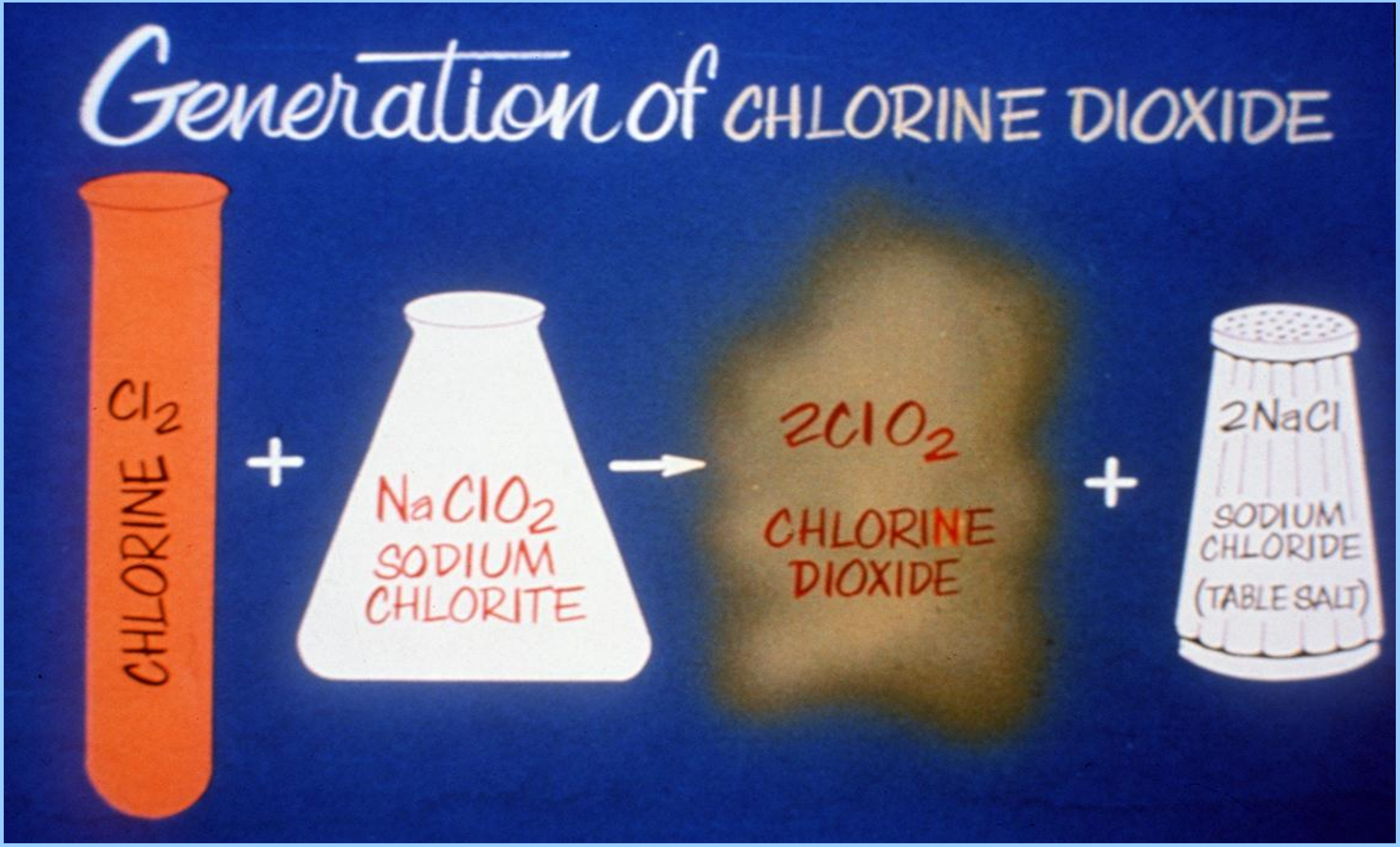
- ***Electrophilic abstraction:***
  - electron transfer from oxidizable species (M) to the oxidant (e.g. $ClO_2 + M \rightarrow ClO_2^- + M_{ox}$
- ***Substitution reactions***
  - halogen is transferred onto organic molecule site replacing hydrogen,
  - Cl^-, Br^- or I^- depending on their presence in source water
- ***Disproportionation:*** decrease in oxidation state,
  - but not by a typical "redox" reaction
  - E.g. $NH_2Cl \rightarrow OCl^-$ (or)
    - $ClO_2 \rightarrow ClO_2^- + ClO_3^-$ at high pH

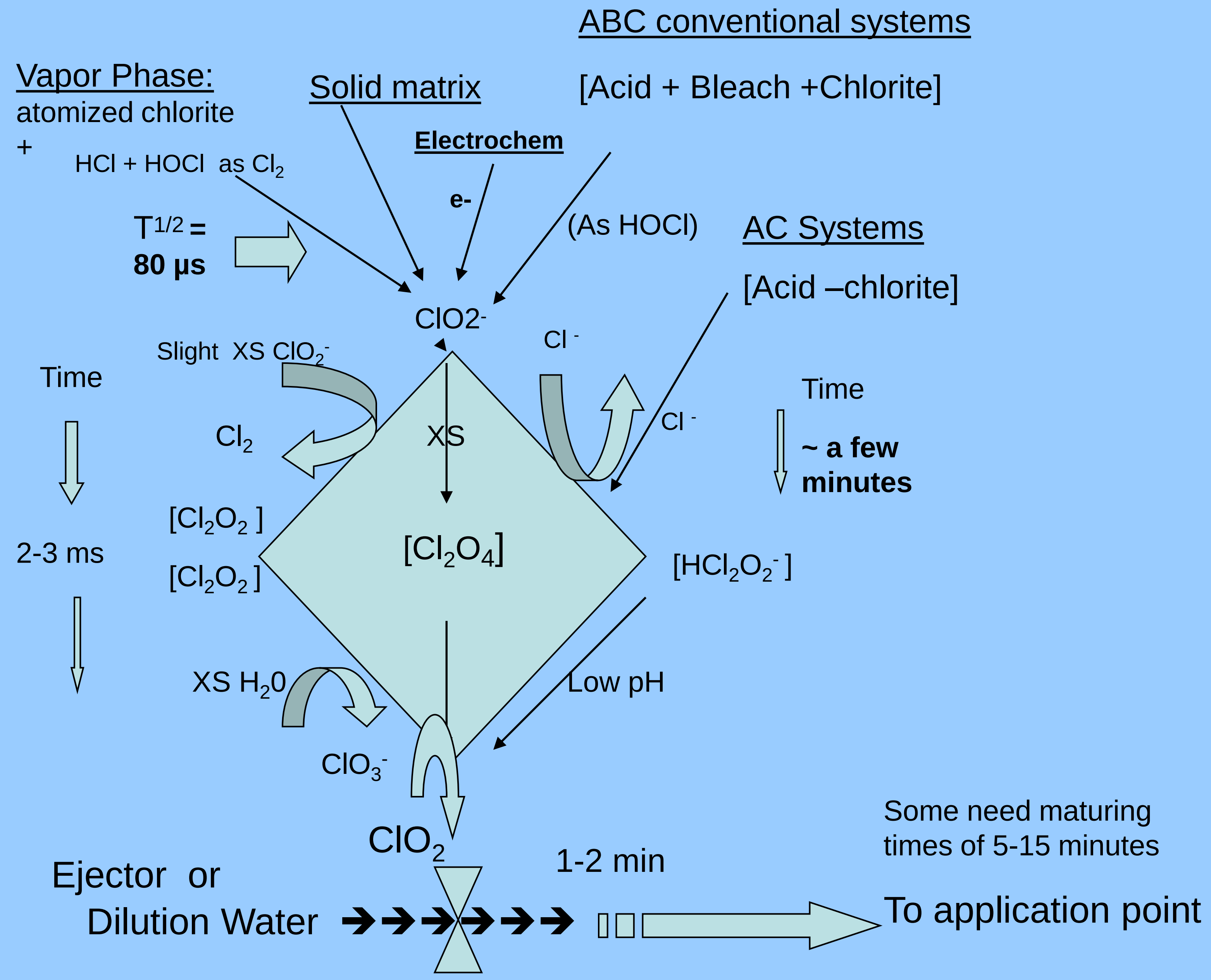
Chlorine Dioxide : ClO_2

- Unstable, uncompressible gas or in pure liquid form
  - must be generated on-site
- Stable free radical, dissolved gas in aqueous solution
  - More Specific oxidation reactions
  - Aka Chlorine peroxide
- Safe concentrations obtained by commercial generators (1-5 g/L)
  - Applied by vacuum injection or pumps (@ 1-2 g/L soln)
  - ➔ ➔ Final doses ~1-1.5 mg/L
- Forms chlorite & chlorate DBP's
- Monitoring requirements
  - Daily ClO_2 leaving plant
  - Daily & monthly chlorite levels



AWWA's Chemistry 101 for ClO_2




ABC conventional systems
Vapor Phase:
atomized chlorite
+
HCl + HOCl as Cl_2
Solid matrix
[Acid + Bleach +Chlorite]
Electrochem
e-
(As HOCl)
AC Systems
$T^{1/2}$ =
80 µs
[Acid –chlorite]
ClO2-
Cl -
Slight XS ClO_2^-
Time
Time
Cl -
Cl_2
XS
~ a few
minutes
$[Cl_2O_2]$
$[Cl_2O_4]$
2-3 ms
$[HCl_2O_2^-]$
$[Cl_2O_2]$
XS H_20
Low pH
ClO_3^-
ClO_2
Some need maturing
times of 5-15 minutes
1-2 min
Ejector or
Dilution Water
To application point

“Unique” ClO_2 Reaction Column under high vacuum, before dilution water

ClO_2 generators

- Dozens of manufacturers & vendors, hundreds of patents
- Primarily Chlorite-based in the drinking water industry
    - 12% - 25% Aqueous chlorite
    - One design uses solid chlorite impregnated into inert matrix
    - Only one chlorate-based, uses peroxide & sulfuric acid
- Production size (ppd) is critical
- 2 or 3 chemical systems
    - Cl_2 gas, bleach and/or acid
    - Recent advancements in electrochemical systems

Precautions

- Ensure proper start-up & training, chlorite safety
  - Fire training & MSDS
    - 2200^{o}C, ➔ ➔ O_2
- Avoid mixtures of acid & chlorite under pressure
  - conditions are extremely dangerous
- Safe Patented Systems
  - Avoid Home-built units like this one!

Ozone generators

- Highly energetic corona discharge from glass dielectric material to SS outer ground
  - across 1-2.5 mm gap with O_2 flow under pressure
  - O_2 activated to intermediates which form ozone
      - but can also degrade ozone
  - factors – pressure, dryness, purity, temp, residence time in gap,
    - Voltage, current intensity & frequency,
  - Production regulated to outside factors
    - pressure, gas flow & power
- Photochemical methods
    - VUV lamps (190-200 nm) –
    - higher energy (ionizing) radiation at lower UV wavelengths

Ozone in water

- Complex generation chemistry (ionized oxygen intermediates)
  - but very user friendly for application in water
  - Same oxy-intermediates also degrade ozone
- Ozone/O_2 mixture is not very soluble
- Boundary layer dynamics must be optimized to transfer O_3 before the bubble escapes.
  - (e.g. not enough transfer area or too short of time.
    - “Hard” or “soft” bubbles
  - Off-gassed ozone must be destroyed above contactors
- counter-current flow patterns for contact chambers increase times
- More efficient diffusers favor high CxT credits for ozone
- New Mazzie ejectors with internal mixing vanes
  - improve solubility and application into process water contact chamber

OZONE & related species - Decomposition in water

• Ozone	O_3
• Hydroxyl radical	$OH\bullet$
• Superoxide radical	O_2^-
- Protonic form	HO_2
• Singlet oxygen	O^-

Aqueous Ozone Reactions

12 OZONE IN WATER TREATMENT

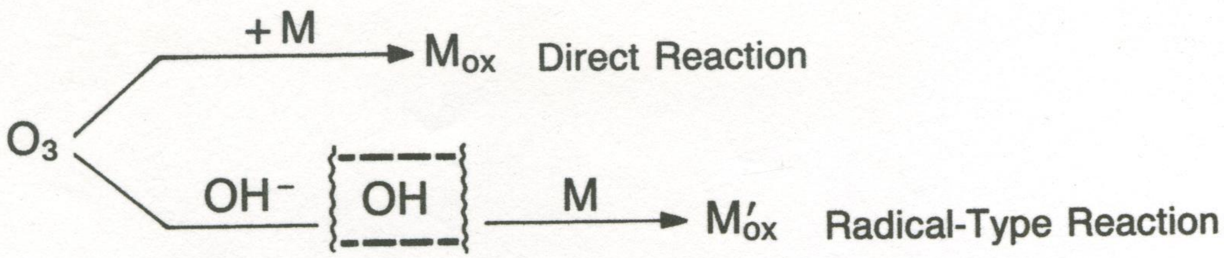


Figure II–1 Reactivity of Ozone in Aqueous Solution

Ozone Demand

- Very different characteristics than the chlorine-based disinfectants.
- Much stronger (but) very non-specific oxidation
- Instantaneous demand must be satisfied, then rapid consumption and decay of O_3 means only short contact times can be established in properly designed contact chambers
- pH and carbonate affect ozone deterioration in solution

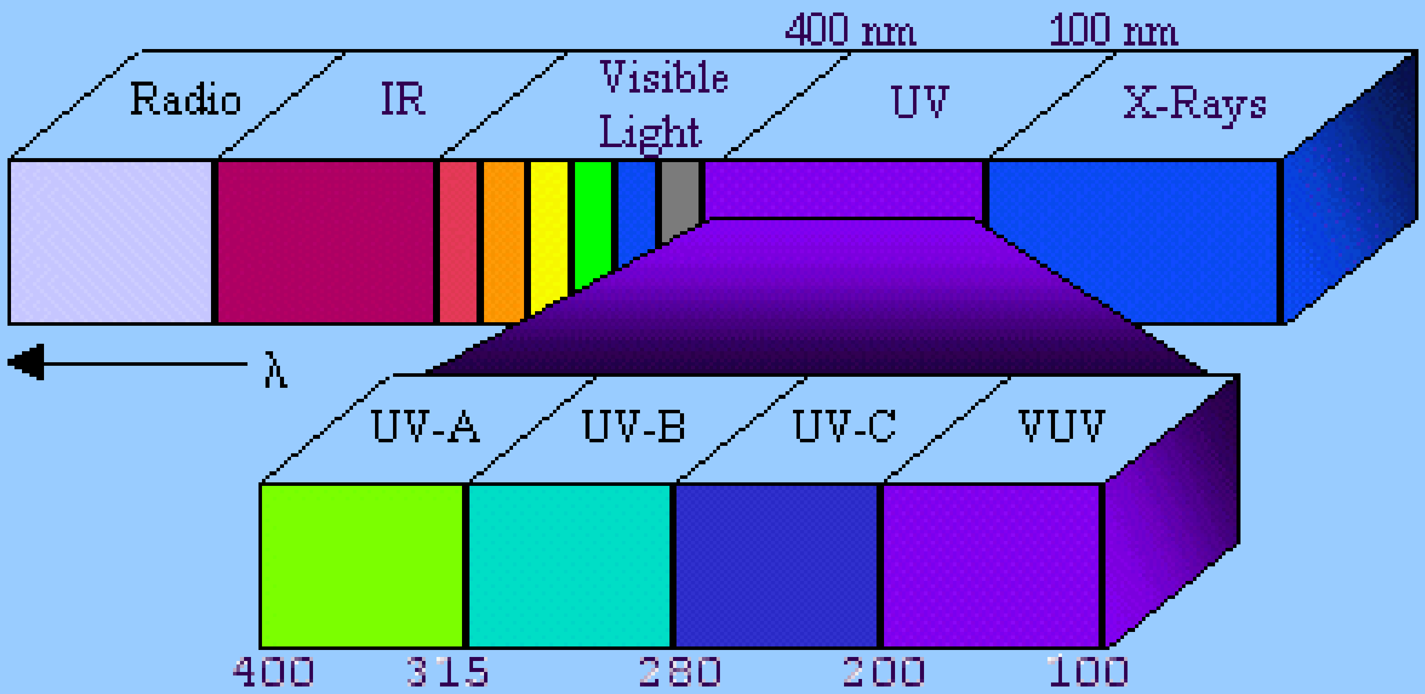
Approved (& Recommended) Monitoring Methods

- **<u>Chlorine & chloramines</u>**
  - "Free" or total chlorine kits
  - DPD, DPD glycine, DPD FAS
  - Amperometric method
  - Iodimetric (starch –iodine)
  - Differential pH activity for MCA
- **<u>Chlorine dioxide</u>**
  - Lissamine Green B (LGB)
    - USEPA method 327, kits
  - Amp titration Method II
    - Method-by-difference
    - APHA Method 4500.ClO2-E
    - Subject to False Positives
- **<u>Ozone</u>**
  - Indigo Tri-Sulphonate (ITS)

- Daily in-plant testing
- Analytical Skills& training
  - On-line detectors
  - e.g. demand studies
  - dosage mass recoveries
  - Feedstock analyses
- Specificity is critical
  - false CxT's a problem!
  - Not so for routine chlorine
- DPD is no longer approved for ClO_2 (too non-specific)
- In-line electronic sensors for continuous CxT credits
  - O_3 & chlorine are good
  - ClO_2 only fair

UV Basics - Electromagnetic Spectrum

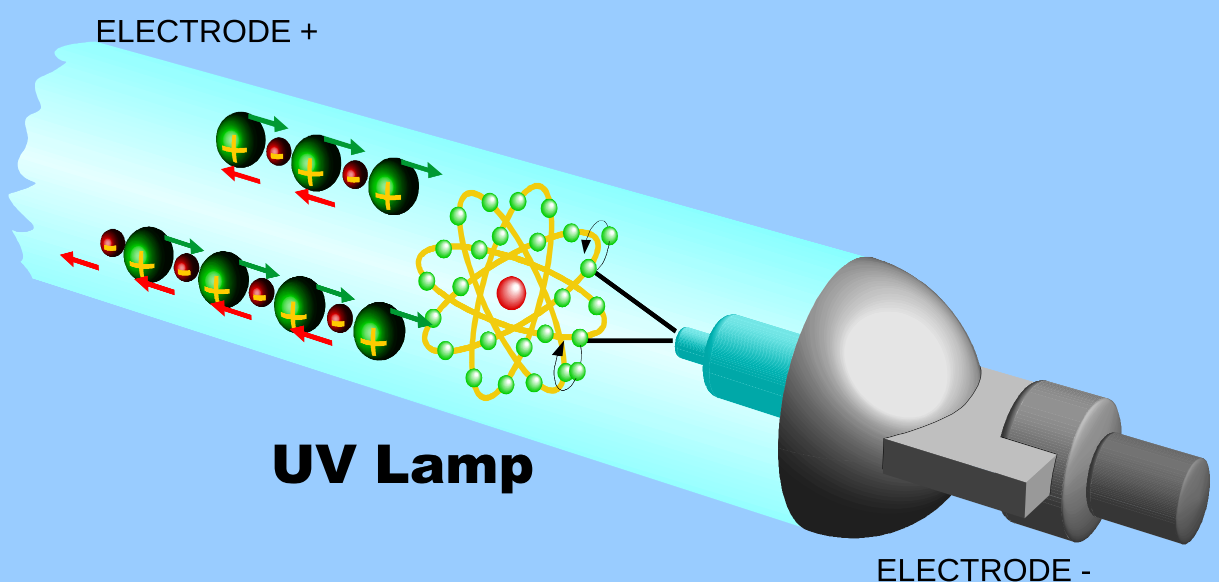
courtesy of Bertrand Dussert, Siemens



Generation of UV_C Light

1) Electrons are accelerated by an electric field through mercury vapor inside lamp

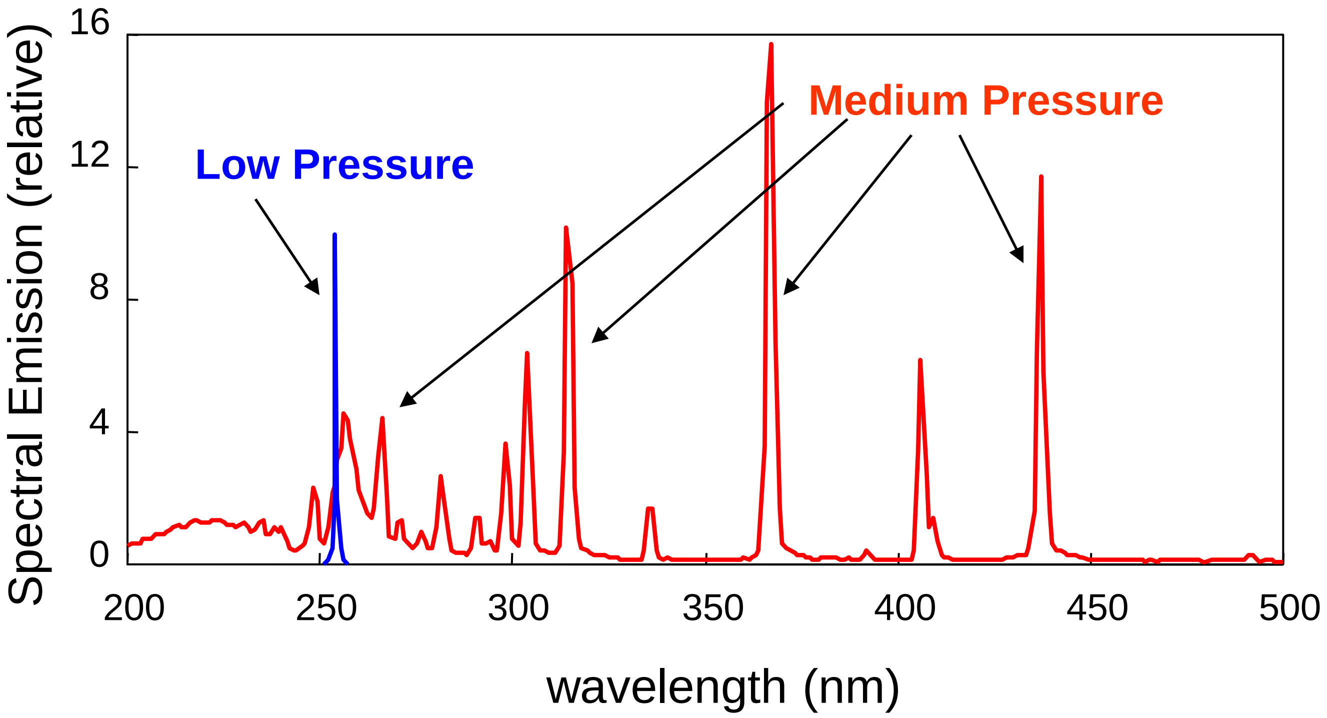
2) Part of them return from excited states to states of lower energy under spontaneous emission of UV radiation



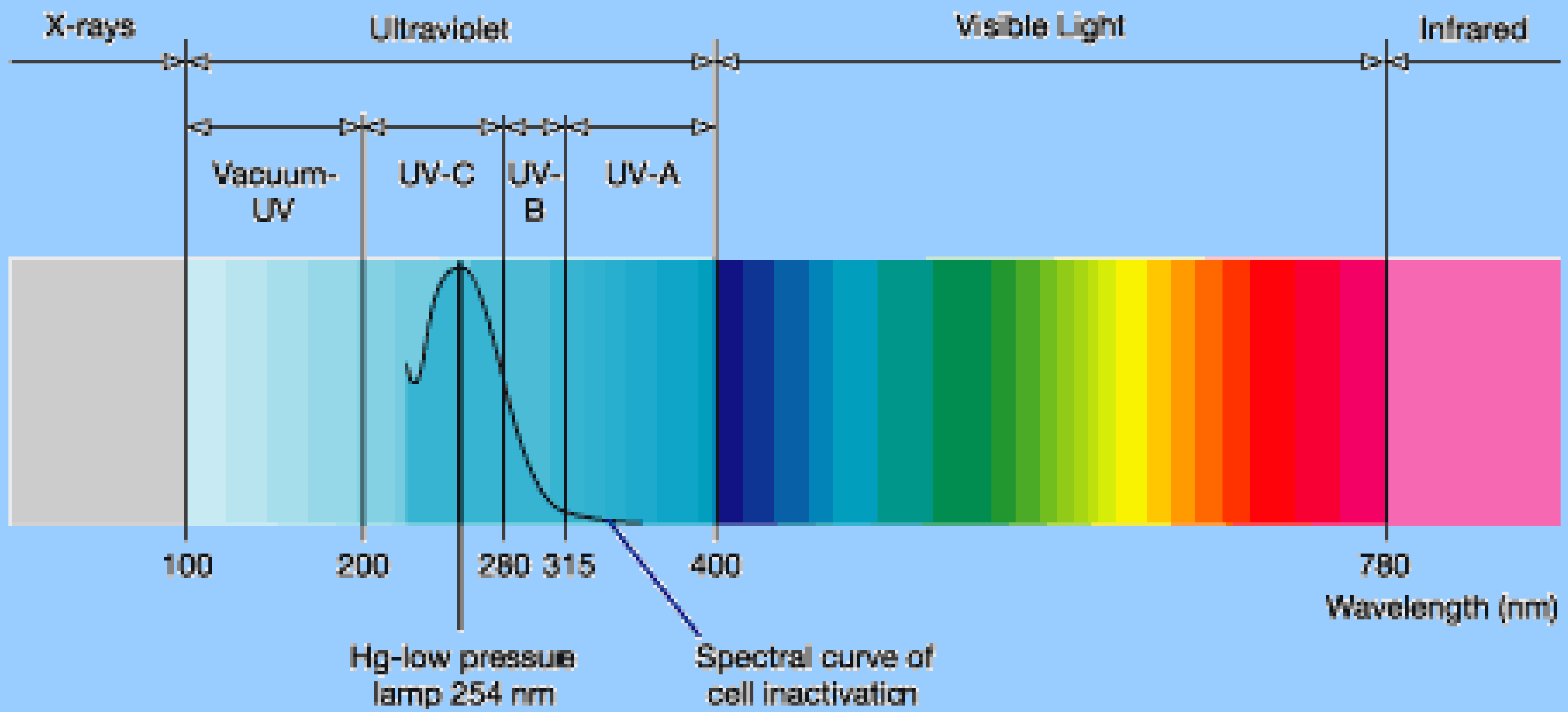
UV “Dose” Terminology

- UV Fluence “Rate” (E’)
  - W/m2 or mW/cm2
  - Total radiant power through a defined target
- UV Fluence “Dose” (H’)
  - as J/cm2 or mJ/cm2
  - Dose is the time integral of the fluence rate,
  - or as total radiant energy at all wavelengths from all directions passing through an infinitely small target of a defined cross section dA

Monochromatic vs. Polychromatic UV Lamps – Spectral Emission



Mechanism of UV Disinfection



Impact of Lamp Technology on Installation, Operation, Performance and Maintenance of a UV System

Selection Criterion	LP/LO	LP/HO	LP Amalgam	MP
Performance – Impact of Water Temperature	High	High	Low	None
Performance - Mechanism	Damages DNA only; risk of photoreactivation			Damages DNA, proteins, enzymes, cell wall, and membrane; greatly eliminates risk of repair More efficient for Adenovirus

UV Lamp Types – Properties

Type	Input Power (W)	UVC Efficiency (%)	Lifetime (Hours or years)
Low Pressure / Low Output	5-80	30-40	8,000-12,000 **(~ 1 - 1.5 yr)**
Low Pressure / High Output	10-150	25-35	8,000-15,000 **(1- 2 yr)**
Low Pressure / Amalgam	40-600	35	8,000-16,000 **(1-2 yr)**
Medium Pressure	400–60,000	10-15	3,000-9,000 **(4 mos- 1 yr)**

UV

Advantages

- Specific contact sites and short times of exposure
- Equipment reliability
- Specific λ mechanisms
- Few DBP's due to non-ionizing radiation power
- Effective for chlorine-resistant protozoan cysts & bacterial spores

Disadvantages

- Intended as add-on protection to other primary disinfectants
- Some anti-microbial questions
  - Regrowth of damaged cells
  - Clumping, virus inactivation
- Dependence - instrumentation
  - No residual "C" measured
  - Methods for confirming or monitoring inactivation
- Attenuation: high turbidity
- Lamp replacement
    - Frequency and cost
    - Planned redundancy
- May affect choice of system

Chlorine

Advantages

- Proven safe & effective technology
- Waterborne disease prevention
- Cheap & reliable
- Application and monitoring ease
- Excellent training & standards of practice

Disadvantages

- X-DBP's
- Storage questions
  - Environmental, urban
  - New DHS reports?
- Chlorine-resistant microbial species & protozoan oocysts
- May contribute chlorate from hypo salts
- Brominated species if bromide present

Chlorine Dioxide

Advantages

- Retrofit capabilities
- Readily available precursors
- Approved monitoring methods
- Many safe systems
  - Mechanical reliability
  - Technical expertise of vendors is in question

Disadvantages

- Must be generated on-site
- More expensive than chlorine
- Volatile gas (e.g. over basins)
- No purity or performance standards
- (C) residuals difficult to measure and maintain - may lead to false CxT’s
- More skill needed for monitoring & analysis ➔ advanced training
- Some Offensive odor events reported
  - (but limited to new carpeting)
- Inorganic DBP’s formed
  - chlorite (regulated)
  - chlorate (still unregulated)
- Most common problems-
  - improperly sized generators!

Ozone

Advantages

- Excellent anti-microbial efficacy
- Short exposure times
- Good analytical methods
- Reasonable scale-up costs
- Industry & Equipment Reliability

Disadvantages

- More costly - power
  - UV Lamp or dielectric replacement costs
- Design:
  - diffusers & contactor chambers
- Dry air gas prep costs or LOX
- Potential for regrowth from AOC produced by oxidation
  - BAF/BAC unit processes to assimilate organics
- Off-gas destruction required
- High bromate if Br- present
- poly-Substituted X-DBP’s

(Mono)chloramine

Advantages

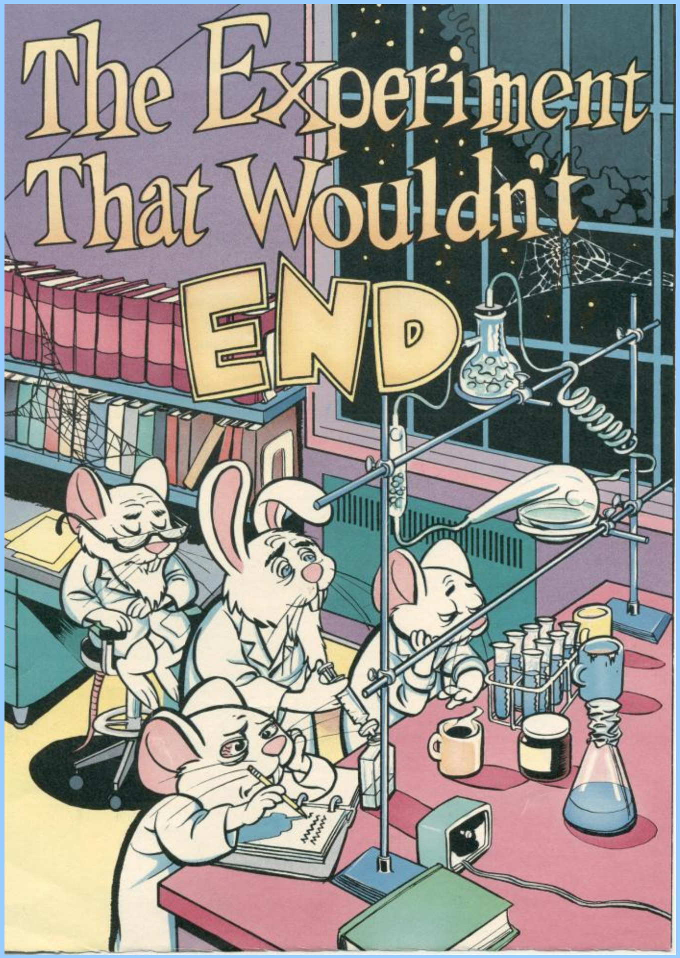
- Inexpensive, retrofit capability
- Spontaneously formed from convenient & safe feedstocks diluted into treatment process stream
- Stable in water due to its low oxidation potential
- Controls most halogenated DBP's
- Controls nuisance in-plant algae
- Controls chlorate (from ClO_2) that may form downstream

Disadvantages

- Low antimicrobial efficacy
  - Extensive contact time needed
- Some DBP formation: research
  - including NDMA & DXAA
- Feedstock relationships are critical under different oxidant demand conditions
- Potential for higher order
  - (i.e. di- and tri- chloramines)
- Additional feedstock chemical
- Potential for nitrification during high DS temperatures

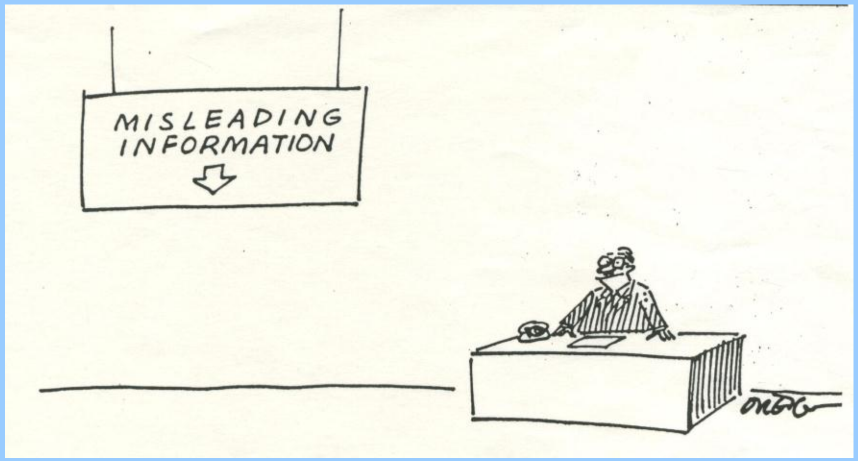
These are not simple choices!

- ***<u>DBP's only part of the story</u>***
- Oxidant applications
- Retrofit capabilities &/or additional costs
- Bench, pilot or in-plant trials ➔ proper design
- Training & experience
- Effective Monitoring
  - not just LED's or ORP



Microbial risks >>>> "chemical" risks from DBP's

Technical advances in analytical detection methods (e.g. low PQL's) for DBP's are much easier and/or quicker to achieve, compared to those improvements we need for actual occurrence levels, risk models or other data used to assess impacts on human health.



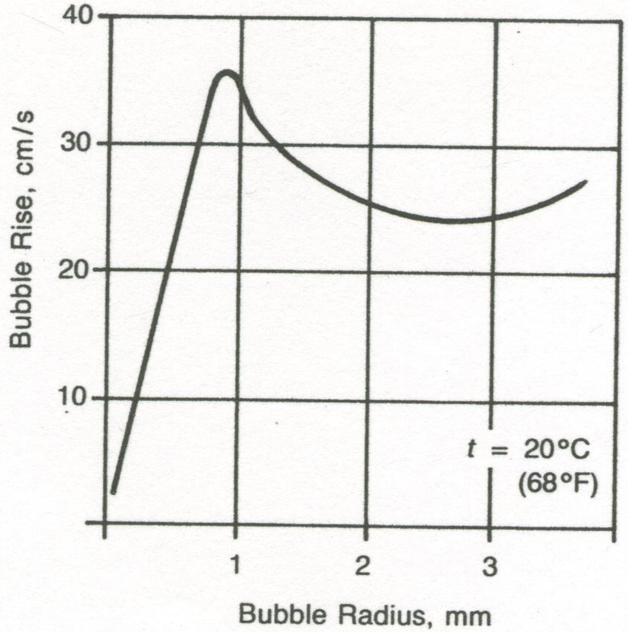
Chlorine Dioxide

- Precursor chlorite requires registration with OPP under FIFRA but the chlorate precursor is still a question?
- Generated ClO_2 equipment - performance and purity is unregulated
  - not certified by NSF 60/61
  - Excess HOCl appears as "false" ClO_2
- Highly soluble gas in water,
  - Boiling Point @ 8°C, volatile
  - subject to air stripping or CO_2
  - injected prior to GAC/PAC
  - Or into rapid mix with lime,
- Does not hydrolyze like chlorine gas (10^6 times slower)
- Not as pH sensitive as chlorine as a disinfectant
- AWWA standard B303(05) for sodium chlorite purity
- NSF certification required for precursors chlorite, hypo (bleach) and acid
- Adequate trials, testing and operator training is essential
- Production size is ***critical*** !

Chemical Terminology - OZONE

- ***Ion radical*** (mostly for ozone species)
  - species has an extra electron for a single negative charge to complete the shell
- ***Direct Ozone or radical oxidation pathway***
  - Two pathways for oxidation by ozone or its radicals formed by decomposition in water

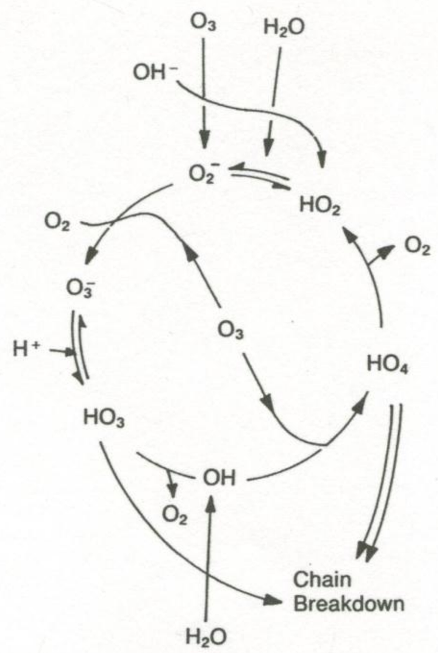
Ozone bubble rise rate



Source: Masschelein (1982a).

Figure II–48 Bubble Rise Velocity as a Function of Dimensions

Ozone decay in water



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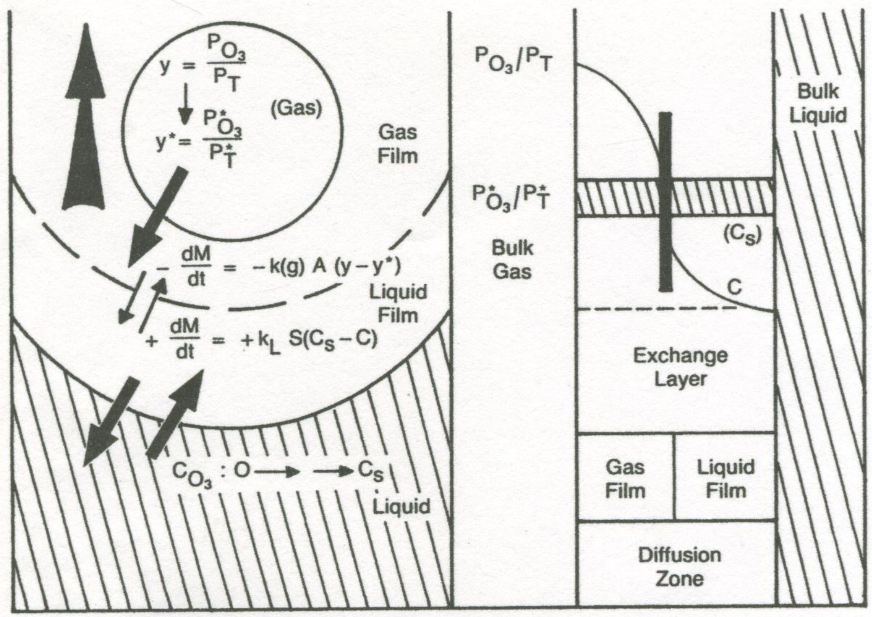
3 Reaction Diagram and Rate Constants for Ozone Decomposition Process

Ozone diffusion boundaries

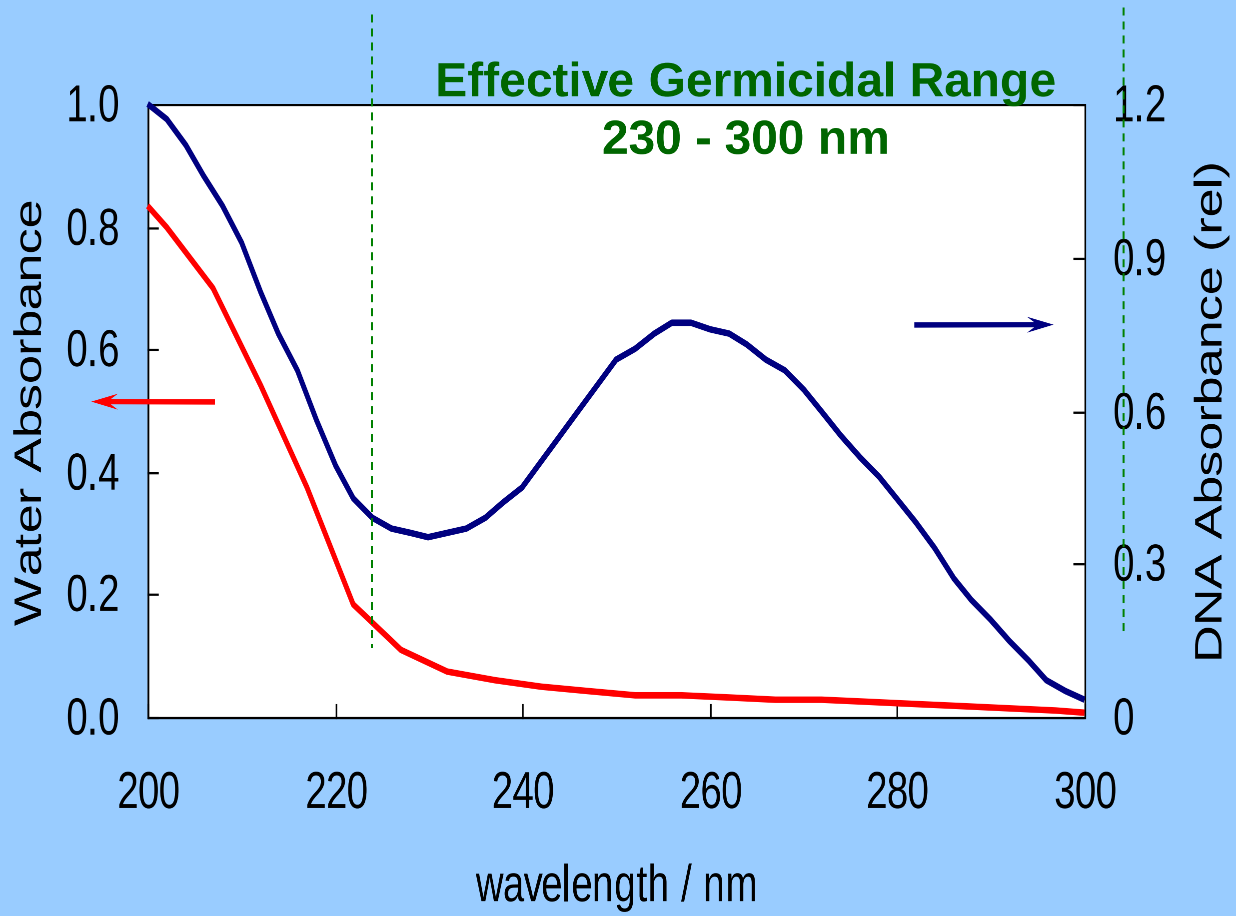


Source: Masschelein (1982a)

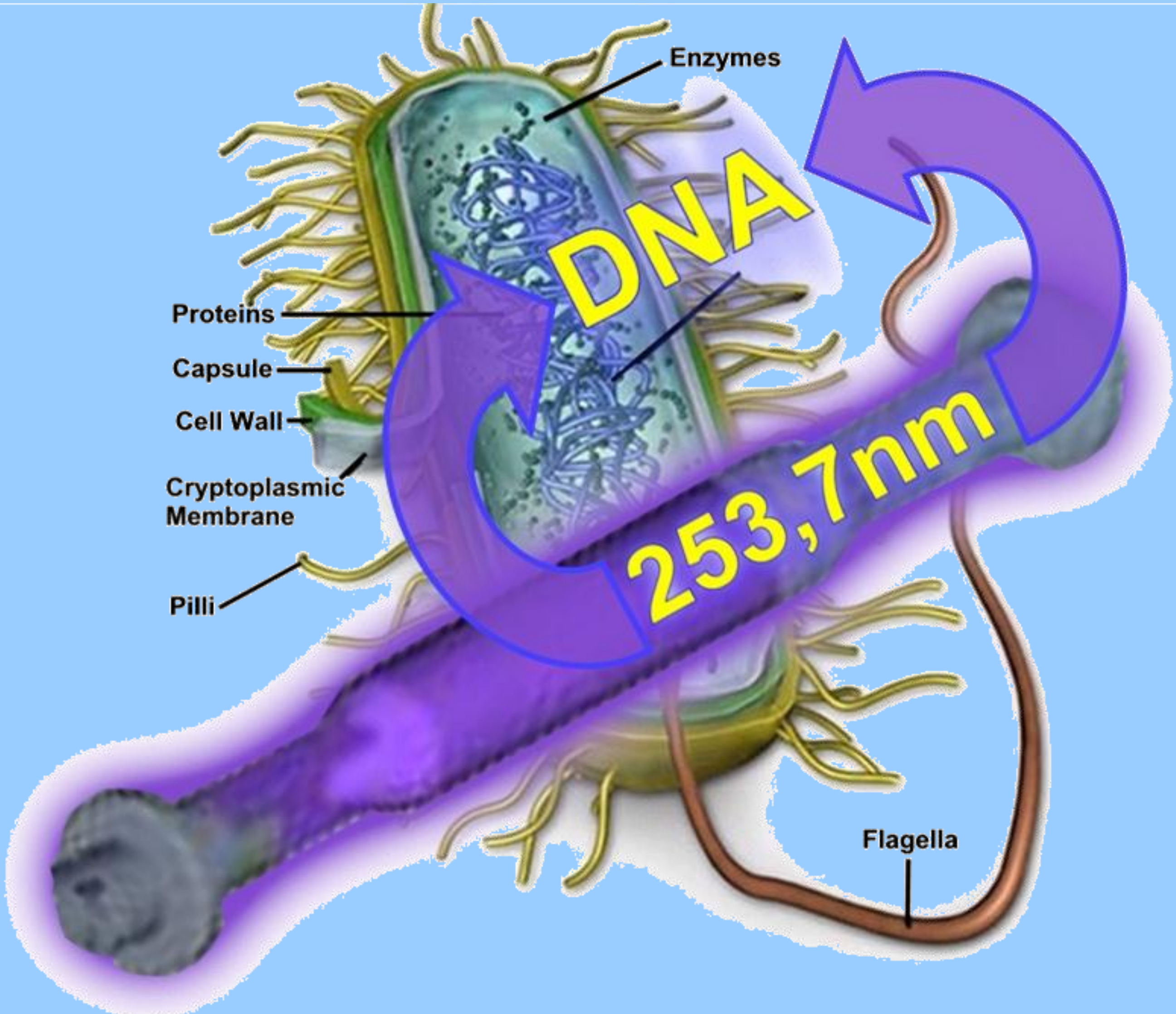
Figure II—47 Schematic of Double-Film Transfer

Germicidal Wavelengths

All UV-C is not created equal



Microbial effect of a low pressure lamp



Microbial effect of a medium pressure lamp